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Photoluminescence of $ZnGa_2O_4$: Mn phosphor fired at vacuum atmosphere

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Abstract

The $ZnGa_2O_4$ phosphor doped with Mn^{2+} was fired from the mixed of ZnO and Ga_2O_3, the effects of firing conditions and the emission characteristics were investigated. $Zn_{1-x}Mn_xGa_2O_4$ phosphors fired at air atmosphere, exhibits two emission bands with main peak at 506 nm (Mn^{2+} emission center) and weak peak at 666 nm (Mn^{4+} emission center). However, where as fired at vacuum atmosphere, the emission spectrum shown only 506 nm peak, and its intensity increase drastically. From its excitation spectrum, apart from 245 nm (the absorption peak of $ZnGa_2O_4$), there are two absorption peaks (304 and 626 nm) which derived from Mn^{2+}, these spectra fit the energy levels of $^4T_1$ (4P) and $^4T_1$ (4G) during Mn^{2+} ($3d^5$) split. The green emission band of 506 nm can be excited by such a absorption peak, the highest intensity is provoked by 304 nm. The emission intensity of $Zn_{1-x}Mn_xGa_2O_4$ phosphors of 506 nm peak are strongest when firing in 10^{-2} Torr vacuum atmosphere at 1300°C, 1.5 h and Mn^{2+} concentration is $x = 0.006$. © 1999 Elsevier Science Limited and Techna S.r.l. All rights reserved.

Keywords: Phosphors; Photoluminescence; Zinc gallate; Vacuum firing

1. Introduction

$ZnGa_2O_4$ phosphors is a spinel structure oxidant, and it has the ability to have emission generated by low voltage electricity. There have been many papers presented in recent years concerning the topic of the emission traits and the processing methods of $ZnGa_2O_4$ phosphors [1–3]. Generalizations of these studies show that in the spinel structure of $ZnGa_2O_4$ phosphors. Zn ions occupy A sites in the tetrahedral crystal lattice, Ga ions occupy B sites in the octahedral crystal lattice, which is a structure very similar to that of the normal spinel structure [4]. Its optical energy level band gap is approximately 4.4 eV, and it has excellent thermal stabilization and electrical conductivity [1], which makes it extremely suitable to serve as illumination material on plane display monitors such as Vacuum fluorescent display (VFD). But it also has defects such as having a wide emission spectrum range, and an inferior degree of color purity and emission intensity [5]. Improvements directed towards these defects may be made through processing methods, or by adding dopants in phosphors.

$ZnGa_2O_4$ phosphors will emit 450∼470 nm of blue light after being excited [1–3], but the emission peak will shift to the long wave side after the phosphors have been doped with certain transition metal elements. For example, those doped with Mn^{2+} change to emitting 506 nm of green light [2,6,7]; those doped with Cr^{3+} emit red light near to 700 nm [8], and phosphors doped with Co^{2+} emit 660 nm of orange–red light [9]. The firing procedure in the process takes place in the air atmosphere because these $ZnGa_2O_4$ phosphors are oxidants. But when the $ZnGa_2O_4$ phosphors are doped with Mn^{2+}, a portion of Mn^{2+} is oxidized into Mn^{4+} and faint orange–red light of 666 nm appears; at the same time this causes the emission intensity of 506 nm to weaken [5]. In order to prevent Mn^{2+} from further oxidation, firing generally takes place in a more protective atmosphere (such as in N_2, Ar, or in vacuum), as in the firing process of MnZn–Ferrite. Apart from this, Shea and Itoh [1] mentioned that if fired $ZnGa_2O_4$ phosphors undergo reduction processing, their emission intensity may be increased [1,2]. But these phosphors also need to have a coating treatment immediately, or else its emission intensity will decrease gradually due to the surface oxidation.

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In papers which discuss the processing methods for oxide phosphors, there are none yet which have reports on firing conducted in protective atmospheres. For this reason, this study focuses on examining the emission characteristics and the firing conditions of $ZnGa_2O_4$ phosphors which are doped with Mn^{2+} and fired in vacuum atmosphere.

2. Experimental procedure

The phosphors compositions of $Zn_{1-x}Mn_xGa_2O_4$ with x ranging from 0 to 0.03 were synthesized via a conventional solid state reaction. Starting powders of high purity ZnO (Cerac Ltd., 200 mesh, 99.999%), Ga_2O_3 (Cerac Ltd., 325 mesh, 99.999%) and dopant $Mn(NO_3)_2{\cdot}2H_2O$ (Aesar Ltd., 99.98%), weighted on an analytical balance to an accuracy of ± 0.1mg, thoroughly mixed for 10 h in Turbula shake mixer with alcohol solvent. The mixed slurry was dried in a hot water bath, then fired at 1200~1300°C in 10^{-2} Torr vacuum atmosphere for 1.5~2 h in a covered alumina crucible to obtain homogeneous phosphor powders.

The grain size of the fired powder were measured by Shimadzu SA-CP3L particle size analyzer and examined in the scanning electron microscope (SEM) using Hitachi S-800 scanning electron microscopy. The phases of the phosphors were characterized by X-ray diffraction (XRD) using Rigaku X-ray diffractometer with CuK_α radiation at 40 kV, 15 mA and 4°(2θ)/min scanning rate.

The photoluminescence emission and excitation spectra of polycrystalline phosphors were obtained using a Shimadzu RF-5301PC spectrofluoro-photometer. The excitation spectra can be obtained from scanning wavelength from 220 to 800 nm monitored at 506 nm. The emission wavelength was scanned from 400 to 700 nm excited at 254, 304 or 626 nm.

3. Results and discussion

3.1. The synthesis of phosphor

The firing temperature of $ZnGa_2O_4$ phosphors through the solid reaction method can be obtained from the results of DTA analysis, the synthetic temperature when the mixed ratio of $ZnO/Ga_2O_3 = 1{:}1$ (mole ratio) is approximately 1050°C. Therefore, in previous studies, there have been cases in which firing conditions were done at 1100°C for long period (over 10 h) [1,2], and there have also been cases in which firing conditions were carried out at 1300°C for a shorter period of time (3~5 h). These firing conditions were all conducted in air atmosphere. In order to understand the process and result of vacuum firing, and to lessen the loss of ZnO, and to save energy consumption, this experiment has shortened the time period in the set of firing conditions to 1.5 or 2 h; the firing temperature is set at 1200 and 1300°C, the vacuum is set at 10^{-2} Torr. The XRD diagram of phosphors obtained from different firing parameters is as shown in Fig. 1. When firing at air atmosphere, 1100°C for 10 h, a pure $ZnGa_2O_4$ phase is obtained. But firing at vacuum atmosphere, 1200°C for 1.5 h, apart from producing spinel structured $ZnGa_2O_4$ phase, there is also a small amount of Ga_2O_3 phase. When firing at 1300°C for 1.5 h, the Ga_2O_3 phase increases obviously. There are two possibilities which explain the existence of the Ga_2O_3 phase here: (1) the synthetic reaction is incomplete (the firing period is shorter), (2) the high vapor pressure of ZnO causes partial ZnO in firings above 1200°C in vacuum to evaporate.

It can be seen from the XRD diagram that for firings in vacuum atmosphere, only Ga_2O_3 phase peaks apart from $ZnGa_2O_4$ phase peaks; there are no ZnO phase peaks. It is then proved through chemical analysis results that the mole ratio of ZnO and Ga_2O_3 after vacuum firing has changed from 1:1 into 0.9:1. Thus, we can see that firing in vacuum will cause partial loss of ZnO through evaporation, and it will also cause the mole ratio between ZnO and Ga_2O_3 to obtain a better emission intensity in the condition of 0.9:1 [3,5].

The particle size of $ZnGa_2O_4$ phosphor powder after firing at 1300°C for 1.5 h is approximately 0.5~1.0 μm; mixed powder which has not gone through firing is 0.3~1.0 μm. The scanning electron micrographs of mixed powder and fired $ZnGa_2O_4$:Mn phosphor are shown in Fig. 2. From this, it can be seen that the growth of particles is limited when firing in vacuum atmosphere, because the firing period is shorter and no fluxes added.

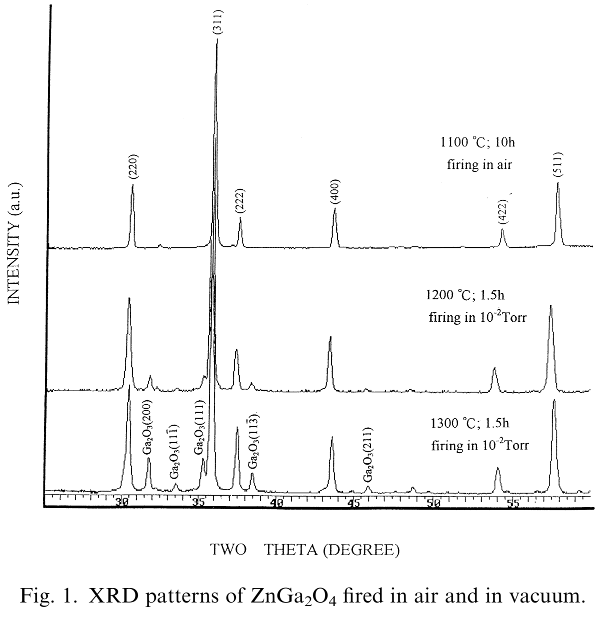

Fig. 1. XRD patterns of $ZnGa_2O_4$ fired in air and in vacuum.

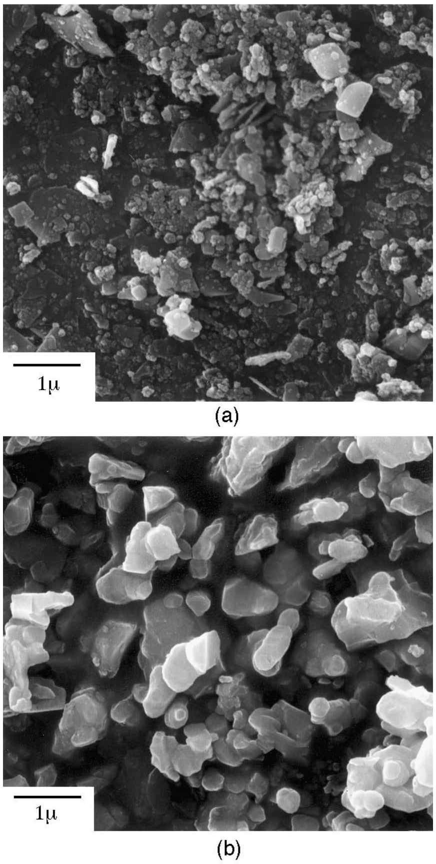

Fig. 2. Scanning electron micrographs of $ZnGa_2O_4$:Mn phosphor: (a) the mixed powder before firing; (b) 1300°C, 1.5 h in 10^{-2} Torr fired.

3.2. Photoluminescence of $ZnGa_2O_4$:Mn phosphors

Spinel structured $ZnGa_2O_4$ phosphor like other wide bandgap semiconductors, it exhibits a strong self-activated fluorescence [10], which will emit 470 nm of blue light after being excited. When Mn^{2+} is added as a activator in the $ZnGa_2O_4$ phosphors, an Mn^{2+} emission center is formed, which causes its emission peak to shift from 470 to 506 nm; green light is emitted, as shown in Fig. 3. The width of its emission spectrum range is also narrowed down half-wave width from 110 to 23 nm, which allows it to obtain a better purity of color.

The preparation of oxide phosphors is usually firing in the air atmosphere. For $ZnGa_2O_4$ phosphors which have been doped with 3d transition metal ions to act as its activator, such as Co^{2+}, Cr^{3+} which have a more stable oxidation may be fired in the air atmosphere. But in the situation when the phosphor have been doped with Mn^{2+}, the Mn^{2+}can be easily oxidized into Mn^{4+} during firing under high temperature, which will then affect the emission characteristics of the Mn^{2+} emission center formed inside $ZnGa_2O_4$. The following is a discussion of the characteristics which the emission spectrum and excitation spectrum of $ZnGa_2O_4$ phosphors doped with Mn^{2+} fired in vacuum atmosphere have.

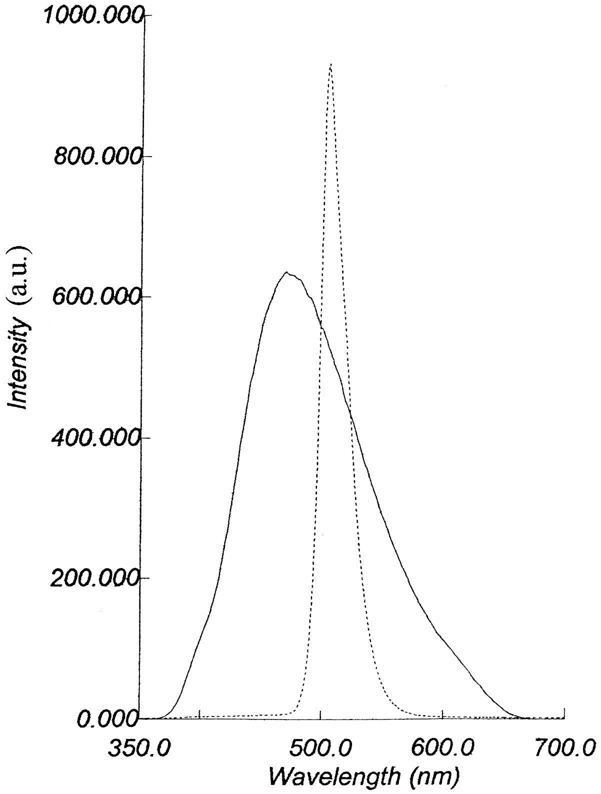

Fig. 3. Emission spectra of $ZnGa_2O_4$ (fired at 1300°C, 5 h in air) and $ZnGa_2O_4$:Mn (fired at 1300°C, 1.5 h in 10^{-2} Torr) phosphors (dotted line: $ZnGa_2O_4$:Mn ($x = 0.006$); solid line: $ZnGa_2O_4$).

3.2.1. Excitation spectrum of $ZnGa_2O_4$:Mn phosphors

The excitation spectrum of $ZnGa_2O_4$:Mn phosphors which have been fired in the vacuum atmosphere and in the air atmosphere is as shown in Fig. 4. Regardless of whether the phosphor is fired in vacuum or in air, the splitting of the Mn^{2+} ($3d^5$) energy level are matched the Tanabe–Sugano energy level diagram. Among these, the intensity of adsorption peaks which have been fired in vacuum are much more stronger than those fired in the air atmosphere, such as 245, 304 and 626 nm. Besides 245 nm being the adsorption peak of $ZnGa_2O_4$ phase [2], 304 and 626 nm also correspond to the $^4T_1$ (4P) and $^4T_1$ (4G) energy level in Mn^{2+} ($3d^5$) splitting. The reason why this result was formed can be derived from $ZnGa_2O_4$ phosphors which have been fired in vacuum: (1) it can be seen from the last XRD diagram that Zn and O are lacking because part of ZnO has been lost through evaporation, (2) there is no sign of the doped Mn^{2+} becoming oxidized into Mn^{4+}, all Mn^{2+} ions substituted Zn^{2+} or occupied its vacancy, (3) due to the lack of Zn–O and the taking over of Mn^{2+}, the entire spinel structure becomes twisted and deformed. Due to this, the electron transition probability among cations (Ga–Mn, Ga–Zn) and between cations and coordinate anions (Ga–O, Mn–O, Zn–O) is improved, and the self-excitation of the host is also increased.

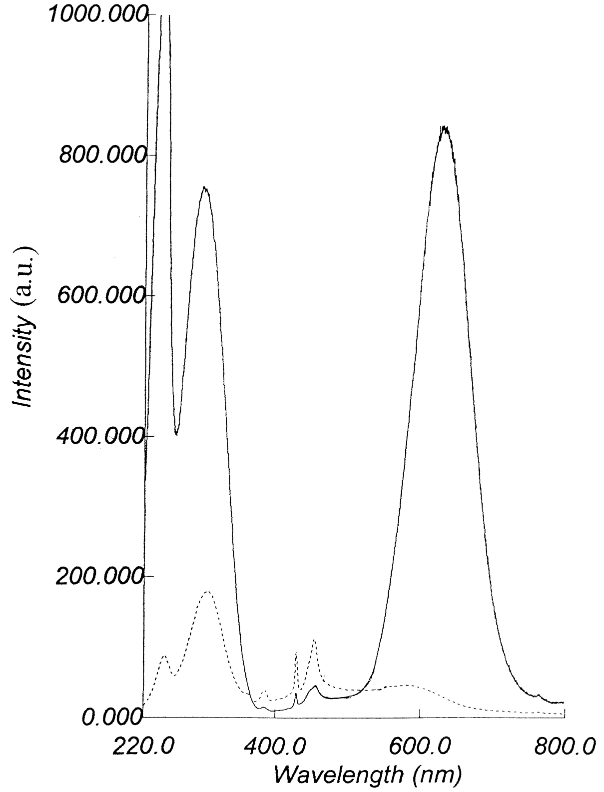

Fig. 4. Excitation spectra of $ZnGa_2O_4$:Mn ($x=0.006$) phosphor fired in air and in 10^{-2} Torr vacuum atmosphere (dotted line: firing in air; solid line: firing in vacuum).

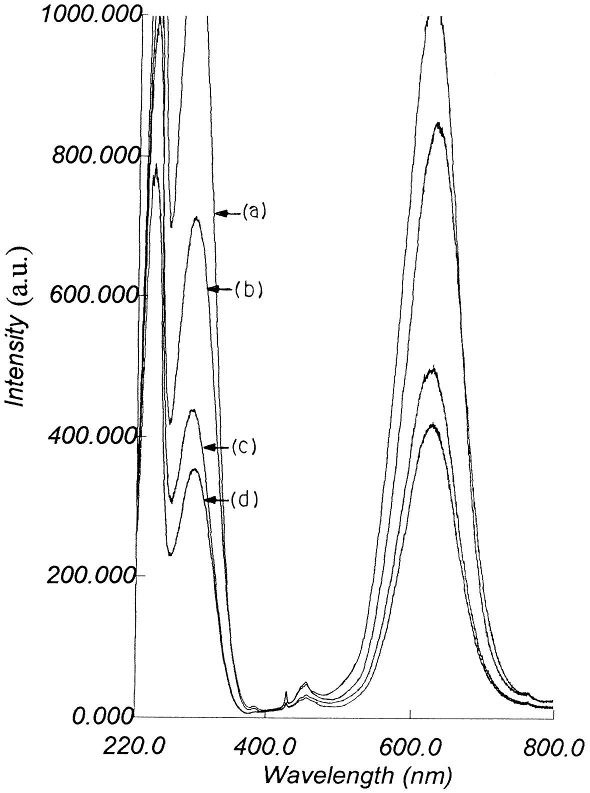

Fig. 5. Excitation spectra of $ZnGa_2O_4$:Mn ($x=0.006$) phosphor fired at various firing condition in 10^{-2} Torr vacuum: (a) 1300°C,1.5 h; (b) 1300°C, 2 h; (c) 1200°C, 2 h; (d) 1200°C, 1.5 h.

The influence which the firing condition in vacuum atmosphere has on its excitation spectrum is shown in Fig. 5. It can be seen from the diagram that the intensity of the excitation spectrum is at its highest when the firing condition at 1300°C for 1.5 h in 10^{-2} Torr vacuum atmosphere.

3.2.2. *Emission spectrum of $ZnGa_2O_4$:Mn phosphors*

Fig. 6 shows the emission spectrum of $ZnGa_2O_4$:Mn ($x=0.006$) phosphors fired in air or in vacuum. It can be seen that each emits green light with a wavelength of 506 nm, and phosphors which have been fired in vacuum have almost 2 times higher emission intensity than fired in air. As for the phosphors which are fired in the air atmosphere, 666 nm of weak orange–red light is produced from the Mn^{4+} emission center because part of Mn^{2+} has been oxidized into Mn^{4+}. The emission intensity of 506 nm has been weakened due to this reason. This green light of 506 nm can not only be excited by 254 nm; it can also be excited from light at 304 and 626 nm wavelengths. Fig. 7 shows the emission spectrum of $ZnGa_2O_4$:Mn ($x=0.006$) phosphor excited by 254, 304 and 626 nm. Apart from the 506 nm main peak in the emission spectrum excited by 254 nm, there will be faint 470 nm light left over from the $ZnGa_2O_4$ host, and the emission intensity of 470 nm weakens with the increase in the concentration of Mn^{2+}. This is because the excitation energy of 254 nm is close to the adsorption peak 245 nm of the $ZnGa_2O_4$ host, part of the excitation energy is absorbed by the $ZnGa_2O_4$ host. The main adsorption peak of Mn^{2+} is 304 nm, and its emission spectrum shows only a simple emission of 506 nm. But as for the 626 nm, the yellow light of 580 nm whose emission is not influenced by the concentration of Mn^{2+} appears apart from the emission of 506 nm. After 580 nm had monitored its adsorption spectrum, it was discovered that the yellow light is scattering light produced at the excitation of 626 nm, and thus it is not influenced by the concentration of Mn^{2+}.

As for the influence which the firing condition in vacuum and the concentration of Mn^{2+} imposes upon the relative emission intensity of 506 nm, the results obtained from 254, 304 and 626 nm are all the same, and are shown in Fig. 8 and Table 1. Among these, the highest intensity are at 1300°C for 1.5 h in 10^{-2} Torr firing condition and Mn^{2+} at a concentration of $x=0.006$.

As previously mentioned that appropriate to the firing condition and the doped concentration of Mn^{+2}, it has obtained apposite structure twisted and the amount ratio of Zn, Mn, and Ga ions. So that, the electron transition among cations (Ga–Zn–Mn) and between cations and coordinate anions (Ga–O, Zn–O, Mn–O) is improved, and self-emission of the host is also

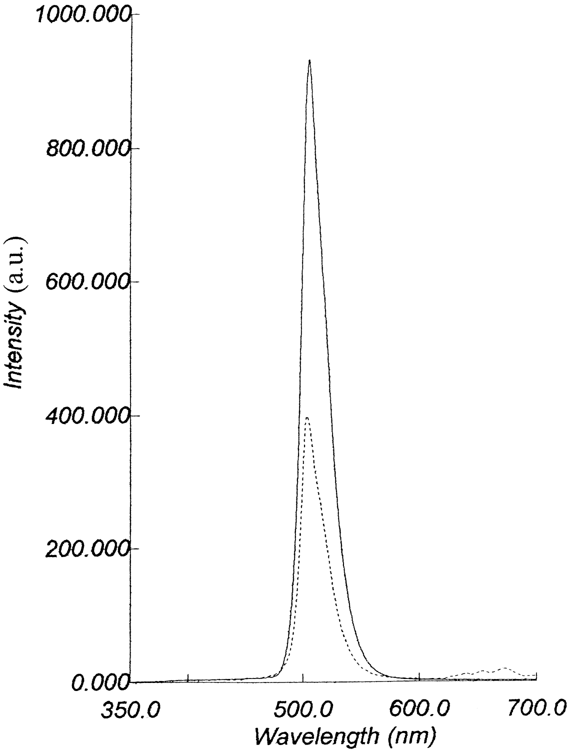

Fig. 6. Emission spectra of $ZnGa_2O_4$:Mn ($x = 0.006$) phosphor fired in air and in 10^{-2} Torr vacuum atmosphere (dotted line: firing in air; solid line: firing in vacuum).

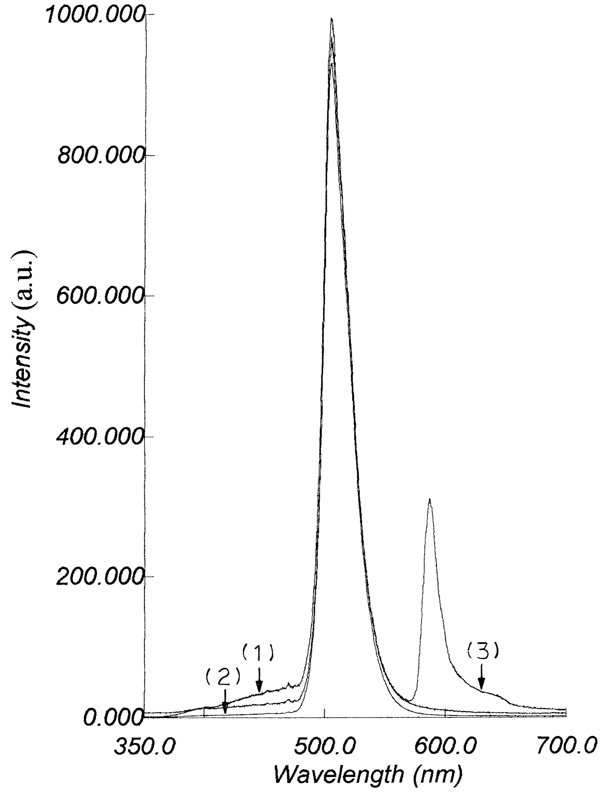

Fig. 7. Emission spectra of $ZnGa_2O_4$:Mn ($x = 0.006$) phosphor excited by 254, 304 and 626 nm: (1) excited by 254 nm; (2) excited by 304 nm; (3) excited by 626 nm.

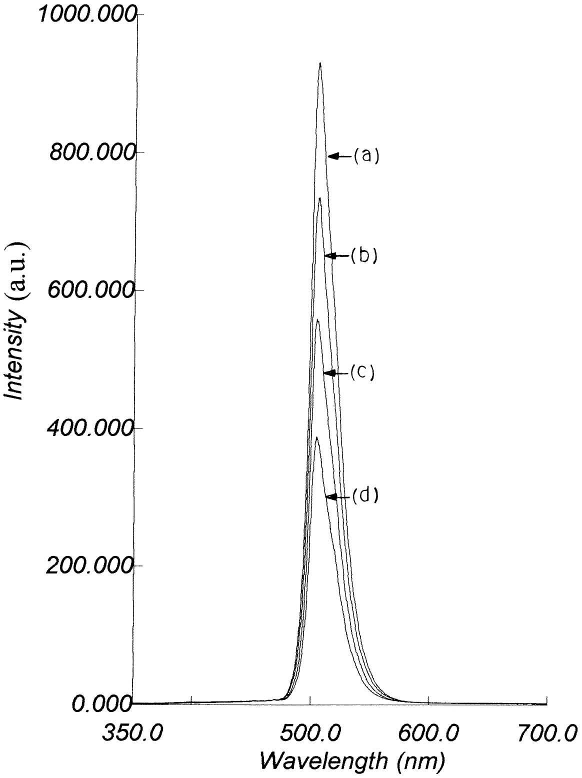

Fig. 8. Emission spectra of $ZnGa_2O_4$:Mn ($x = 0.006$) phosphor fired in vacuum atmosphere (10^{-2} Torr) but different firing temperature and time: (a) 1300°C, 1.5 h; (b) 1300°C, 2 h; (c) 1200°C, 2 h; (d) 1200°C, 1.5 h.

Table 1
Effect of Mn^{2+}concentration on $ZnGa_2O_4$:Mn phosphors emission intensity fired at 1300°C for 1.5 h in 10^{-2} Torr atmosphere

Samples	$Zn_{1-x}Mn_xGa_2O_4$ (x value)	Relative emission intensity (%)
A	0.002	45
B	0.004	54
C	0.006	100
D	0.008	89
E	0.01	80
F	0.02	10

increased. When the doped amount of Mn^{2+} is higher than $x = 0.02$, its intensity decreases evidently that is a result of concentration quenching.

4. Conclusion

The excitation spectrum of $Zn_{1\text{-}x}Mn_xGa_2O_4$ phosphors fired in vacuum atmosphere can be fit the split energy level of Mn^{2+} ($3d^5$), among these the two adsorption peaks 304 and 626 nm each comply to the $^4T_1$ (4P) and $^4T_1$ (4G) energy levels, and their intensity is much more higher than those fired in the air atmosphere.

Apart from 254 nm, the 506 nm green light produced from the Mn^{2+} emission center may also be excited by 304 and 626 nm. For those excited by 254 nm, apart from the main emission peak of 506 nm, there are residual weak emissions of 470 nm from the host. For those excited by 626 nm, there is 580 nm of weak emissions. Only those excited by 304 nm show pure emissions of 506 nm. The emission intensity of 506 nm is influenced by the firing condition and the concentration of Mn^{2+}, the best results are produced when firing at 1300°C for 1.5 h in 10^{-2} Torr and doped amount of Mn^{2+} is $x = 0.006$.

Acknowledgements

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